at predominantly each polymer chain end are functional groups.

23. The polymer of claim 21, wherein the thermally stable groups can be modified to be used in subsequent chemical reactions.

24. A block copolymer comprising two or more blocks of units obtained from free radically (co)polymerizable monomers, wherein the block copolymer has a residue from an initiator at one chain end and, at the other end of the polymer chain, a member selected from the group consisting of radically transferable atoms, radically transferable groups, groups formed by conventional chemistry on said radically transferable atoms and groups formed by conventional chemistry on said radically transferable groups.

25. The block copolymer as claimed in claim 24, wherein said radically (co)polymerizable monomers are selected from the group consisting of polar and non-polar monomers.

26. A symmetrical block copolymer, comprising units obtained from one or more radically (co)polymerizable monomers, having a residue from an initiator in the polymer chain and, at each chain end, a member selected from the group consisting of radically transferable atoms, radically transferable groups, groups obtained by conventional chemistry from said radically transferable atoms and groups obtained by conventional chemistry from said radically transferable groups.

27. A symmetrical copolymer comprising units obtained from free radically (co)polymerizable monomers, wherein the symmetrical copolymer is formed by coupling two polymer chains, such that substantially each polymer chain has a residue of an initiator present on substantially each polymer chain end.

28. A copolymer comprising units obtained from two or more free radically (co)polymerizable monomers, wherein the copolymer is a statistical, periodic or sequential copolymer and exhibits controlled molecular weight distribution and known functionality on predominantly each of the polymer chain ends.

29. A copolymer comprising units obtained from one or more free radically (co)polymerizable monomers and formed by using an initiator having more than two radically transferable atoms or groups, wherein the copolymer has three or more polymer chains emanating from a residue of the initiator contained in the copolymer and each of these polymer chains has at the polymer chain end a member selected from the group consisting of radically transferable atoms, radically transferable groups, groups formed by conventional chemistry from said radically transferable atoms and groups formed by conventional chemistry from said radically transferable groups.

30. A copolymer comprising units obtained from two or more radically (co)polymerizable monomers wherein the copolymer has a composition that changes in a controlled manner along the length of the polymer chain from terminus to terminus.

31. The (co)polymer as claimed in claim 21, wherein said (co)polymer is a polystyrene having a residue from a free radical initiator at the head of each polymer chain and a radically transferable group at the tail of each polymer chain end.

32. The block copolymer as claimed in claim 24, wherein said block copolymer is a poly(Styrene-block-Methyl Acrylate) copolymer having a residue of an initiator molecule at an initiation site at one polymer chain end, and a radically transferable group at the other polymer chain end.

33. The symmetrical block copolymer as claimed in claim 26, wherein the symmetrical block copolymer is a poly(Styrene-block-Methyl Acrylate-block-Styrene)

copolymer having a radically transferable atom or group at each polymer chain end.

34. The (co)polymer as claimed in claim 21, wherein said (co)polymer is a member selected from the group consisting of linear, monofunctional, star and telechelic polystyrenes, linear and star poly(methyl acrylate)s, poly(butyl acrylate)s, poly(methyl methacrylate)s, and polyisoprenes, wherein the (co)polymer has either an identifiable specific head group or a residue of an initiator at an initiation site, and a radically transferable atom or group at a polymer chain end, displays a tacticity of a polymer prepared by free radical polymerization and has a controlled molecular weight distribution.

35. The (co)polymer claimed in claim 28, prepared by (co)polymerizing styrene and methyl acrylate or (co)polymerizing styrene and methyl methacrylate to yield polymers in which the (co)polymer has a composition that changes in a predictable, or calculable, manner from one end of the polymer chain to the other end of the polymer chain.

36. The (co)polymer claimed in claim 30, prepared by (co)polymerizing styrene and methyl acrylate or (co)polymerizing styrene and methyl methacrylate to yield polymers in which the (co)polymer has a composition that changes in a predictable, or calculable, manner from one end of the polymer chain to the other end of the polymer chain.

37. A (co)polymer, exhibiting a stereochemistry and microstructure (as defined by tacticity and sequence distribution) of a polymer formed by a free radical polymerization process and displaying a controlled molecular weight distribution and calculable number average molecular weight, having the formula

$$R^{11}R^{12}R^{13}C\text{–}(M^1)_p\text{–}(M^2)_q\text{–}X$$

$$R^{11}R^{12}R^{13}C\text{–}(M^1)_p\text{–}(M^2)_q\text{–}(M^3)_r\text{–}X$$

$$R^{11}R^{12}R^{13}C\text{–}(M^1)_p\text{–}(M^2)_q\text{–}(M^3)_r\text{–}...\text{–}(M^4)_s\text{–}X$$

wherein X is selected from the group consisting of Cl, Br, I, OR^{10}, SR^{14}, SeR^{14}, O-

$N(R^{14})_2$, S–C(=S)$N(R^{14})_2$, H, OH, N_3, NH_2, COOH, $CONH_2$, and groups that can be formed therefrom by conventional chemical processes, where

R^{10} is an aryl, an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R^{14} is aryl or a straight or branched C_1-C_{20} alkyl group, and where an $N(R^{14})_2$ group is present, the two R^{14} groups may be joined to form a 5- or 6-membered heterocyclic ring,

R^{11}, R^{12} and R^{13} are each independently selected from the group consisting of H, halogen, C_1-C_{20} alkyl C_4-C_8 cycloalkyl, C(=Y)R^5, C(=Y)NR^6R^7, COCl, OH, CN, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C_1-C_6 alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C_1-C_6 alkyl substituted with from 1 to 3 substituents selected from the group consisting of C_1-C_4 alkoxy, aryl, heterocyclyl, C(=Y)R^5, C(=Y)NR^6R^7, oxiranyl and glycidyl, where

R^5 is aryl or an alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R^6 and R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring, such that no more than two of R^{11}, R^{12} and R^{13} are H, and

M^1, M^2, M^3,... up to M^4 are each a radically (co)polymerizable monomer selected such that the monomers in adjacent blocks are riot identical, and p, q, r,... up to s are independently selected such that the number average molecular weight of each block is up to 250,000 g/mol;

the following formulas:

$$X–(M^2)_q–(M^1)_p–(R^{11}R^{12}C)–(M^1)_p–(M^2)_q–X$$

$$X–(M^3)_r–(M^2)_q–(M^1)_p–(R^{11}R^{12}C)–(M^1)_p–(M^2)_q–(M^3)_r–X$$

$$X–(M^4)_s–\,.\,–(M^3)_r–(M^2)_q–(M^1)_p–(R^{11}R^{12}C)–(M^1)_p–(M^2)_q–(M^3)_r–\,.\,–(M^4)_s–X$$

wherein R^{11}, R^{12}, X, M^1, M^2, M^3, ... up to M^4, and p, q, r,... up to s are as defined above;

or the formulas:

$$R^{11}R^{12}R^{13}C–(M^1–M^2)_p–(M^2–M^1)_q–(M^1–M^2)_r–...–(M^v–M^y)_s–X$$

$$(R^{11}R^{12}R^{13}C)–[(M^1–M^2)_p–(M^2–M^1)_q–(M^1–M^2)_r–...–(M^v–M^y)_s–X]_z$$

where R^{11}, R^{12}, R^{13} and X are as defined above,

M^1 and M^2 are different radically-(co)polymerizable monomers, and M^v is one of M^1 and M^2 and M^y is the other of M^1 and M^2, and

Z is from 2 to 6

p, q, r,... up to s are independently selected such that the number average molecular weight of the copolymer is up to 1,000,000 g/mol;

of the formulas:

$$(R^{11'}R^{12'}R^{13'}C)–[(M^1)_p–(M^2)_q–X]_z$$

$$(R^{11'}R^{12'}R^{13'}C)–[(M^1)_p–(M^2)_q–(M^3)_r–X]_z$$

$$(R^{11'}R^{12'}R^{13'}C)–[(M^1)_p–(M^2)_q–(M^3)_r– ...– (M^4)_s–X]_z$$

where $R^{11'}$, $R^{12'}$, and $R^{13'}$ are the same as R^{11}, R^{12} and R^{13} with the proviso that $R^{11'}$, $R^{12'}$, and $R^{13'}$ combined contain from 2 to 5 X groups, where X is as defined above;

M^1, M^2, M^3, ... M^4 are as defined above; and

z is from 3 to 6; and

of the formula:

$$R^{11}R^{12}R^{13}C–(M^1_aM^2_b)–(M^1_cM^2_d)–(M^1_eM^2_f)– ... –(M^1_gM^2_h)–(M^1_iM^2_j)–X$$

$$R^{11}R^{12}R^{13}C–[(M^1_aM^2_b)–(M^1_cM^2_d)–(M^1_eM^2_f)– ... –(M^1_gM^2_h)–(M^1_iM^2_j)–X]_z$$

where R^{11}, R^{12}, R^{13} and X are as defined above, M^1 and M^2 are different radically-polymerizable monomers, z = 2 to 6 and a, b, c, d, e, f, ... up to i and j are non-negative numbers independently selected such that a + b = c + d = 100, and any or all of (e + f), (g +

h) and (i + j) 100 or 0, wherein the a:b ratio is from 100:0 to 0:100, the c:d ratio is from 95:5 to 5:95, such that c < a and d > b, and where applicable, the e:f ratio is from 90:10 to 10:90, such that e < c and f > d, and the endpoints of the molar ratio ranges of first monomer to second monomer in successive blocks progressively decrease or increase by 5 such that the e;f ratio is from 5:95 to 95:5, such that e ≠ c and f ≠ d, and the i:j ratio is from 0:100 to 100:0, such that i ≠ e and j ≠ f.

38. The (co)polymer of Claim 37, having a formula:

$$R^{11}R^{12}R^{13}C–(M^1)_p–(M^2)_q–X$$

$$R^{11}R^{12}R^{13}C–(M^1)_p–(M^2)_q–(M^3)_r–X \text{ or}$$

$$R^{11}R^{12}R^{13}C–(M^1)_p–(M^2)_q–(M^3)_r–...–(M^4)_s–X$$

wherein X is selected from the group consisting of Cl, Br, I, OR^{10}, SR^{14}, SeR^{14}, O-$N(R^{14})_2$, S-C(=S)$N(R^{14})_2$, H, OH, N_3, NH_2, COOH and $CONH_2$; and where

R^{10} is aryl, alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R^{14} is aryl or a straight or branched C_1–C_{20} alkyl group, and where an $N(R^{14})_2$ group is present, the two R^{14} groups may be joined to form a 5- or 6-membered heterocyclic ring,

R^{11}, R^{12} and R^{13} are each independently selected from the group consisting of H, halogen, C_1-C_{20} alkyl, C_3-C_8 cycloalkyl, C(=Y)R^5, C(=Y)NR^6R^7, COCl, OH, CN, C_2–C_{20} alkenyl, C_2–C_{20} alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C_1–C_6 alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C_1–C_6 alkyl substituted with from 1 to 3 substituents selected from the group consisting of C_1–C_4 alkoxy, aryl, heterocyclyl, C(=Y)R^5, C(=Y)NR^6R^7, oxiranyl and glycidyl, where

R^5 is aryl, alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms,

aryloxy or heterocyclyloxy; and R^6 and R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring, such that no more than two of R^{11}, R^{12} and R^{13} are H, and

M^1, M^2, M^3, ... up to M^4 are each a radically polymerizable monomer selected such that the monomers in adjacent blocks are not identical, and p, q, r,... up to s are independently selected such that the number average molecular weight of each block is from 1,000 to 250,000 g/mol.

39. The (co)polymer of Claim 37, having a formula:

$$X–(M^2)_q–(M^1)_p–(R^{11}R^{12}C)–(M^1)_p–(M^2)_q–X$$

$$X–(M^3)_r–(M^2)_q–(M^1)_p–(R^{11}R^{12}C)–(M^1)_p–(M^2)_q–(M^3)_r–X \text{ or}$$

$$X–(M^4)_s– .. –(M^3)_r–(M^2)_q–(M^1)_p–(R^{11}R^{12}C)–(M^1)_p–(M^2)_q–(M^3)_r– . –(M^4)_s–X$$

wherein R^{11}, R^{12}, X, M^1, M^2, M^3, ... up to M^4, and p, q, r,... up to s are as previously defined.

40. The (co)polymer of Claim 37, having a formula:

$$R^{11}R^{12}R^{13}C–(M^1M^2)_p–(M^2M^1)_q–(M^1M^2)_r– ... –(M^v–M^y)_s–X \text{ or}$$

$$R^{11}R^{12}R^{13}C–[(M^1M^2)_p–(M^2M^1)_q–(M^1M^2)_r– ... –(M^v–M^y)_s–X]_z$$

wherein z is from 2 to 6;

where R^{11}, R^{12}, R^{13} and X are as previously defined,

M^1 and M^2 are different radically-polymerizable or copolymerizable monomers, and M^v is one of M^1 and M^2 and M^y is the other of M^1 and M^2, and

p, q, r,... up to s are independently selected such that the number average molecular weight of the copolymer is from 1,000 to 1,000,000 g/mol.

41. The (co)polymer of Claim 37, having a formula:

$$(R^{11'}R^{12'}R^{13'}C)–[(M^1)_p–(M^2)_q–X]_z$$

$$(R^{11'}R^{12'}R^{13'}C)–[(M^1)_p–(M^2)_q–(M^3)_r–X]_z \text{ or}$$

$$(R^{11'}R^{12'}R^{13'}C)–[(M^1)_p–(M^2)_q–(M^3)_r– ...– (M^4)_s–X]_z$$

where $R^{11'}$, $R^{12'}$, and $R^{13'}$ are the same as R^{11}, R^{12} and R^{13} as previously defined, with the proviso that $R^{11'}$, $R^{12'}$, and $R^{13'}$ combined contain from 2 to 5 X groups, where X is as defined above;

M^1, M^2, M^3, ... M^4 are as defined above; and

z is from 3 to 6.

42. The (co)polymer of Claim 37, having the formulae:

$$R^{11}R^{12}R^{13}C–(M^1_aM^2_b)–(M^1_cM^2_d)–(M^1_eM^2_f)– ... –(M^1_gM^2_h)–(M^1_iM^2_j)–X$$

$$R^{11}R^{12}R^{13}C–[(M^1_aM^2_b)–(M^1_cM^2_d)–(M^1_eM^2_f)– ... –(M^1_gM^2_h)–(M^1_iM^2_j)–X]_z$$

where R^{11}, R^{12}, R^{13} and X are as previously defined, M^1 and M^2 are different radically-polymerizable or copolymerizable monomers, and a, b, c, d, e, f, ... up to i and j are non-negative numbers independently selected such that a + b = c + d = 100, and any or all of (e + f), (g + h) and (i + j) 100 or 0, wherein the a:b ratio is from 100:0 to 0:100, the c:d ratio is from 95:5 to 5:95, such that c < a and d > b, and where applicable, the e:f ratio is from 90:10 to 10:90, such that e < c and f > d, and the endpoints of the molar ratio ranges of first monomer to second monomer in successive blocks progressively decrease or increase by 5 such that the e;f ratio is from 5:95 to 95:5, such that e ≠ c and f ≠ d, and the i:j ratio is from 0:100 to 100:0, such that i ≠ e and j ≠ f, and

z = 2-6.

43. A graft or comb shaped copolymer in which either or both the backbone polymer or graft copolymer are copolymers prepared from free radically (co)polymerizable monomers

with predetermined molecular weight and controlled molecular weight distribution.

36 44. A hyperbranched, dendritic copolymer prepared by a free radical polymerization process.

45. A polymer of the formula:

$$R^{11}R^{12}R^{13}C–(M^1)_p–X$$

$$X–(M^1)_p–(R^{11}R^{12}C)–(M^1)_p–X$$

$$(R^{11'}R^{12'}R^{13'}C)–[(M^1)_p–X]_z$$

wherein X is selected from the group consisting of Cl, Br, I, OR^{10}, Sr^{14}, SeR^{14}, O-$N(R^{14})_2$, S-C(=S)$N(R^{14})_z$, H, OH, N_3, NH_2, COOH and $CONH_2$, where

R^{10} is an aryl or an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R^{14} is aryl or a straight or branched C_1-C_{20}, alkyl group, and where an $N(R^{14})_2$ group is present, the two R^{14} groups may be joined to form a 5- or 6-membered heterocyclic ring,

R^{11}, R^{12} and R^{13} are each independently selected from the group consisting of H, halogen, C_1-C_{20} alkyl, C_3-C_8 cycloalkyl, C(=Y)R^5, C(=Y)R^5, C(=Y)NR^6R^7, COCl, OH, CN, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C_1-C_6 alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C_1-C_6 alkyl substituted with from 1 to 3 substituents selected from the group consisting of C_1-C_4 alkoxy, aryl, heterocyclyl, C(=Y)R^5, C(=Y)NR^6R^7, oxiranyl arid glycidyl, where

R^5 is aryl, alkyl of from 1 to 20 Carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R^6 arid R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring,

such that no more than two of R^{11}, R^{12} and R^{13} are H and

z is from 3 to 6 and,

the polymer exhibits a stereochemistry characteristic of a free radical polymerized material in conjunction with a controlled molecular weight distribution.

46. The atom transfer radical polymerization process as claimed in claim 1, wherein the initiator is an oligomer or polymer prepared by an atom transfer radical polymerization process.

47. The atom transfer radical polymerization process as claimed in claim 1, wherein the polymerization is carried out in bulk, in solution, in dispersion, in suspension, in an emulsion, in the gas phase, under pressure or under vacuum.

48. The atom transfer radical polymerization process as claimed in claim 47, wherein said polymerization is carried out in solution in a supercritical fluid.

49. The atom transfer radical polymerization process as claimed in claim 1, wherein one or more (co)polymerizable monomers are added sequentially proportionally or continuously to the reaction.

50. The atom transfer radical polymerization process as claimed in claim 1, further comprising adding further initiator to the polymerizing mixture such that the (co)polymer formed has a molecular weight distribution that is broadened by the adding of the further initiator.

51. The atom transfer radical polymerization process as claimed in claim 1, wherein the initiator is prepared by chemical modification of an existing polymer.

52. The atom transfer radical polymerization process as claimed in claim 1, wherein the transition metal is selected from the group consisting of copper, iron, nickel or ruthenium.

53. The atom transfer radical polymerization process as claimed in claim 1, wherein

either or both of the initiator or radically (co)polymerizable monomer contains, or is capable of generating, an unconjugated ethylene or acetylene moiety.

54. An atom transfer radical polymerization process as claimed in claim 1, wherein the initiator is formed by the reaction of a free radical of the structure I*, with a radically transferable atom or group X' from a transition metal compound of the structure M_t X'n where the transition metal, M_t, is in a higher of two available oxidation states,

I* is a substituted C, S, 0, N, or any other atom that can form a free radical when stabilized and is formed in-situ conventionally, such that the initiator for the reaction of claim 1, formula (II) or (III) or a mixture thereof, is formed by transfer of a radically transferable group from the transition metal compound to the compound I*

I-X (II)

or,

I-(M)-X (III)

and can be used in-situ or isolated.--

SUPPORT FOR AMENDMENTS

New claims 21-54 have been added in this application. These claims are believed supported by the specification and the claims as originally fiiled. No new matter has been added by these amendments.

Applicants submit that the application is now ready for examination on the merits and early notification of such action is earnestly solicited.

Respectfully submitted,

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